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(19) (CA) **CANADIAN PATENT** (12)

(54) CRACKING CATALYST COMPOSITION

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The present invention relates to catalytic compositions which are used to crack high molecular weight hydrocarbons into products of lower molecular weight, and more specifically, to a catalyst composition which will economically convert sulfur and/or heavy metal containing feedstocks including residual petroleum fractions into products such as gasoline and heating oil.

In recent years the petroleum refining industry  
10 has placed considerable emphasis on the cracking of high molecular weight feedstocks to optimize the production of gasoline and heating oil products. In order to meet the demand for these products, increasing amounts of feedstocks which contain relatively high levels of sulfur and/or heavy metals have been subject to catalytic cracking processes.

It is generally known that cracking catalysts tend to lose desirable activity and selectivity characteristics when contaminated with heavy metals  
20 such as nickel and vanadium. Furthermore it is observed that the catalytic cracking of high sulfur feedstocks results in the emission of ecologically unacceptable amounts of sulfur oxides ( $SO_x$ ). It is also noted that recent environment regulations have limited the quantities of carbon monoxide which may be placed into the atmosphere by way of catalytic cracker regenerator stack gas emissions.

It has been previously suggested that the  $SO_x$  emissions from catalyst crackers may be reduced through

modification of the catalyst in a manner which retains the sulfur within the product feed stream of the unit.

U.S. 3,835,031 to Bertolacini describes a magnesium/calcium containing catalyst which retains sulfur during regeneration in a catalytic cracking unit.

South African Patent 74/4642 to Schwartz describes a catalytic cracking catalyst composition which contains minor quantities of noble metals such as platinum and palladium that serve to oxidize carbon monoxide to carbon dioxide during catalyst regeneration in a catalytic cracker.

U.S. 3,944,482 to Mitchell discloses the preparation of catalyst compositions which possess preferred pore volume characteristics which enable the catalysts to withstand the deactivating effects of relatively large quantities of heavy metals such as mickel and vanadium.

U.S. 3,501,264 to Pilato et al discloses that alkalized alumina ( $\text{Na}_2\text{Al}_2\text{O}_4$ ) is an effective adsorbent for sulfur dioxide which may be used to remove sulfur compounds from flue gases.

It is also noted that commercial catalytic cracking catalysts are available which possess characteristics which enable hydrocarbon processors to control carbon monoxide emissions and to handle residual oil feedstocks in a relatively economical manner. However, to date a commercial catalyst is not available to the industry which controls  $\text{SO}_x$  and carbon monoxide emissions and in addition is capable of withstanding the deactivating effects of heavy metal containing feedstocks.

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It is therefore an object of the present invention to provide an improved catalytic cracking catalyst composition which will reduce the CO and SO<sub>x</sub> emissions from catalytic cracking units.

It is further object to provide a catalyst which will economically and efficiently catalytically crack residual oil feedstocks which contain high levels of heavy metals such as nickel and vanadium.

It is still another object to provide a catalytic  
10 cracking catalyst composition which may be used to process a variety of sulfur and/or heavy metal containing feedstocks to produce high yields of gasoline fractions while controlling or reducing ecologically unacceptable CO and SO<sub>x</sub> emissions.

Broadly, our present invention contemplates a catalytic cracking composition which comprises a rare earth exchanged crystalline aluminosilicate zeolite, clay, and alumina bound into a composite with an inorganic oxide sol and/or silica-alumina hydrogel  
20 binder and containing from about 0.1 to 20 parts per million platinum and/or palladium.

More specifically, we have found that a highly active catalytic cracking catalyst which is capable of effectively cracking sulfur and/or metal containing hydrocarbon feedstocks and in addition controlling the amount of CO and SO<sub>x</sub> emissions from a commercial cat cracker may be prepared by combining the following components:

1. From about 12 to 60% by weight of a rare earth  
30 exchanged crystalline aluminosilicate zeolite preferably Type Y zeolite.

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2. From about 0 to 75% by weight clay.
3. From about 5 to 60% by weight alumina.
4. From about 15 to 40% by weight of an inorganic oxide binder.
5. From about 0.1 to 20 parts per million of a noble metal, preferably platinum and/or palladium.

The above noted components may be combined to form a finely divided particulate catalyst composition by the following typical preparation method:

- 10        1. An acidic inorganic oxide sol binder is prepared by mixing a sodium silicate solution with an inorganic acid such as sulfuric and/or an acid salt solution such as aluminum sulfate solution to produce a sol having a pH of from about 2.9 to 4.0.
2. The clay and alumina is added to the sol or to the sol forming components.
3. The zeolite component is slurried with water with pH adjustment of from 3.5-4.5 if required.
- 20        4. The sol/clay/alumina mixture and the zeolite slurry is combined to form a spray drier feed having a pH of from about 2.9 to 4.0.
5. The spray drier feed mixture is then spray dried to form a particulate catalyst which is washed and/or ion exchanged to remove soluble salts such as sodium and sulfate, and exchanged with rare earth ions if the zeolite was not previously rare earth exchanged.

The spray dried composition which has been washed to  
30 remove soluble salts may then be impregnated with a solution of platinum and/or palladium salts to impart the desired

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concentration of noble metal. It is also contemplated that the platinum ingredient may be added in the form of a separate platinum impregnated additive such as platinum impregnated mullite, alumina or silica-alumina microspheres having a particle size and density similar to that of the zeolite-containing catalyst.

The rare earth exchanged zeolite used in the practice of the present invention is preferably a rare earth exchanged Type Y zeolite. The rare earth exchanged Type Y zeolite may  
10 comprise a calcined rare earth exchanged zeolite such as the so-called CREX and CREY zeolites disclosed in U. S. Patent 3,402,996 to McDaniel. It is also contemplated that thermally stabilized zeolites such as Z-14-US as disclosed in U. S. 3,293,192 to Maher may be utilized when exchanged in the rare earth form, i.e., Z-14-US RE. Furthermore, it is contemplated that the Z-14-US zeolite in combination with a calcined rare earth exchanged zeolite (CREY), i.e., Z-14-US/CREY, may be utilized and/or combinations of CREY and NaY, wherein the NaY is subsequently exchanged via an exchange of the spray  
20 dried catalyst. Also the partially rare earth exchanged calcined Type Y zeolite disclosed in U. S. Patent 3,607,043 (PCY) or the rare earth hydrogen exchanged zeolite (REHY) disclosed in U. S. Patent 3,676,368 may be utilized.

In general the type of rare earth exchanged zeolite utilized in the preparation of the catalyst will be determined by the selectivity characteristics which are desired in the final catalysts. For example, where it is desired to produce high yields of  $C_3$  and  $C_4$  olefins which tend to increase the octane rating of the gasoline fractions produced,  
30 it is generally found that Z-14-US RE, Z-14-US in combination

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with CREY, or PCY zeolite is preferred. Furthermore, where it is contemplated that the catalyst is to be utilized to process heavy residual oil feedstocks which contain substantial quantities of heavy metals such as nickel and vanadium, it is generally preferred to use a rare earth exchanged zeolite Type Y zeolite (REY) which contains from about 11 to 22% by weight rare earth ions. Furthermore, where it is desired to obtain a particularly high degree of  $SO_x$  control in the regenerator stack gas emissions of the catalytic cracker and residual cracking capabilities it is generally preferred to utilize a zeolite such as CREY.

The clay component of the catalyst may comprise raw kaolin clay or a thermally modified or acid treated clay such as metakaolin, as well as other clays such as chlorite.

The alumina ingredient of the presently contemplated catalyst is preferably added to the catalyst in the form of free alumina hydrate which is commercially available from many sources. The free alumina hydrate is generally referred to as  $\alpha$ -trihydrate. It is also contemplated that the alumina may be added in the form of a silica-alumina hydrogel which contains 12 to 80% by weight alumina. It is contemplated that the presence of alumina in these catalysts in conjunction with the sieve content, rare earth and sodium level, along with a noble metal, performs as an  $SO_x$  adsorber and converter during thermal/oxidative regeneration of the catalyst and retains the sulfur compounds as sulfur oxides during the regeneration part of the catalytic cracking cycle. The regenerated catalyst is recycled and returned to the cracking zone wherein the sulfur compounds are reduced to hydrogen sulfide which is collected in the product stream from the catalyst cracker and

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subsequently separated by fractionation and/or adsorbing means.

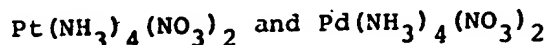
The inorganic sol binder which may be used to prepare the present catalyst is generally described as an acid sol binder which is prepared in accordance with the procedures set forth in U. S. 3,867,308 to Elliott and 3,957,689 to Ostermaier. The Elliott and Ostermaier patents also clearly set forth general procedures which may be used to prepare the catalyst of the present invention.

The catalyst contemplated herein will contain minor quantities, that is from about 0.1 to 20 parts per million, of a noble metal such as platinum and/or palladium. It is found that the presence of this minor quantity of noble metal serves to oxidize carbon monoxide to carbon dioxide in the regenerator section of the catalytic cracker. Furthermore, it is found that the presence of the platinum and palladium is critical in the control of the  $SO_x$  emissions which evolve through the stack gas of the regenerator section of the catalytic cracker. It is found that when the sulfur containing components which are carried from the cracking zone of the unit to the regenerator unit by way of sulfur rich carbon formed on the spent catalyst the presence of platinum in the regenerator section promotes the oxidation of the sulfur compounds to  $SO_3$  which combines with the alumina and other metal oxides present, such as rare earth and sodium oxide, to form a stable form of sulfur which is not removed from the regenerator along with the stack gases. The  $SO_4$  containing regenerated catalyst is then returned to the reducing zone, i.e., hydrogen atmosphere of the cracking zone, and the  $SO_4$  is reduced and hydrolyzed to hydrogen sulfide which remains in the product stream of the catalytic cracker.



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In general, the noble metal-component is preferably added by way of impregnating the spray dried and washed catalyst composition with a dilute solution of the platinum and/or palladium salt such as



Typically the impregnation procedure is conducted by spraying the catalyst composition with a solution of the desired metal salt.

The catalyst of the present invention possesses a high degree of activity for the cracking of hydrocarbons. Furthermore, the catalysts can be designed to be particularly selective for the production of gasoline fractions of increased octane by means of selecting the desired zeolite promoter. Furthermore, as discussed above, the catalysts are resistant to poisoning by heavy metal, nickel and vanadia components which are present in residual oil fractions. Also the catalysts may be used to effectively control the  $\text{SO}_x$  and fuel emissions from commercial catalytic cracking units.

The catalysts of our invention generally possess a surface area of from about 100 to 550  $\text{m}^2/\text{g}$  and a pore volume of from about 0.1 to 0.5.

Having described the basic aspects of our invention the following examples are given to illustrate specific examples thereof:

#### Example I

A silica sol bound catalyst was prepared following a procedure similar to those set forth in U. S. Patent 3,957,689 to Ostermaier and Elliott. A buffered silica hydrosol binder was prepared as follows:

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An acid alum solution was prepared by adding 8.03 liters of an  $\text{Al}_2\text{SO}_4$  solution containing 84 gr of  $\text{Al}_2\text{O}_3$ /liter to 12.78 liters of a 18°Bé solution of sulfuric acid. In the resulting solution 40 percent of the hydrogen ion equivalents are present as aluminum  $\text{Al}^{+++}$ .

The acid alum solution was pumped to a high speed mixer at a rate of 555 cc per minute where it was mixed with an 18°Bé sodium silicate solution having an  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio of 3.25. The silicate solution had been fed to the mixer at the rate of 1.5 10 liter per minute. The resulting hydrosol had a pH between 2.5 and 3.0 and had an excess of 20 percent of the acid-aluminum sulfate necessary to neutralize the  $\text{Na}_2\text{O}$  present in the silicate.

To prepare 10,000 g of finished catalyst (dry basis) 3500 grams of alpha-alumina trihydrate was added to 30,000 g silica-alumina sol. After mixing was complete 3500 g of CREY zeolite in 10 l of deionized water (pH adjusted to 4.0 with dilute sulfuric acid) was added with good agitation to the sol plus  $\text{Al}_2\text{O}_3$  slurry.

After 5-10 minutes of vigorous agitation the result- 20 ing slurry was spray dried in a typical pilot plant type spray drier (6 ft. diameter Bowen-2 fluid nozzle drier). The spray dried material was washed with ammonium sulfate to remove  $\text{Na}_2\text{O}$ , water washed to remove excess sulfate, and dried; the final composition consisting of 35% CREY, 30%  $\text{SiO}_2$  and 35%  $\text{Al}_2\text{O}_3$  as  $\alpha$ -trihydrate.

Prior to testing for residual cracking and  $\text{SO}_x$  reduction capability, a requisite amount of the dried catalyst was impregnated with a dilute solution of  $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$  to yield a platinum content on the finished 30 catalyst of 3 ppm. The impregnated material was compared

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with commercial grade catalysts for its metal tolerance using microactivity testing procedure wherein the catalysts were combined with various amounts of deactivating metals which comprised a mixture of 2 moles V per mole Ni. The activity of the catalysts was determined using the procedure of Ciapetta & Henderson, Oil & Gas Jour., Oct. 16, 1967, pp. 88 to 93. The metal tolerance data for this example are summarized in Table I, which clearly shows the dramatic improvement over the standard catalyst.

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Table I

Selectivity Data For  
Catalysts At Various Metals Levels

Catalyst	Metal Content: wt. % (Ni/V: 1/2)	Standard				Example I			
		0	0.5	1.0	2.0	0	0.5	1.0	2.0
Conv.: Vol %		70	46	32	22	86	81	69	48
H <sub>2</sub> : t %		0.04	0.44	0.58	0.60	0.39	0.36	0.39	0.30
Coke: t. % Fresh Feed		2.2	2.8	2.7	3.0	4.0	4.4	3.6	2.3

Deactivation : 1350°F, 100% steam, 15 psig, 8 hrs.

Test Conditions : 16 WHSV, 3 c/o, 900°F

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Example II

A catalyst was prepared using the procedure of Example I. However, the zeolite was NaY and the spray dried catalyst was exchanged with a rare earth chloride solution to a level of 7.5% by weight  $RE_2O_3$  after ammonium sulfate washing. After the rare earth exchange the catalyst was further washed with water (to remove excess chloride) and dried.

Example III

10 A catalyst was prepared by combining silica hydrosol binder, alpha-alumina trihydrate with a silica-alumina gel which contains 80%  $Al_2O_3$  material. The final composition of the finished catalyst was as follows:

25%  $Al_2O_3$  ( $\alpha$ -trihydrate), 27% (80%  $Al_2O_3$ , 20%  $SiO_2$  gel), 25% NaY and 23%  $SiO_2$  (as binder).

The composition was spray dried, washed with ammonium sulfate, exchanged with rare earth chloride to a level of 4.5% by weight  $RE_2O_3$  and impregnated with 3 ppm

20 platinum.

Example IV

A catalyst was prepared by the procedure of Example I, however, the zeolite input consisted of 17% NaY and 12% 2-14-US sieves (U.S. Patent 3,293,192 to Maher and McDaniel) with 25%  $Al_2O_3$  as  $\alpha$ -trihydrate, 16% kaolin clay and 30%  $SiO_2$  as binder.

After spray drying, the catalyst was washed with ammonium sulfate, exchanged with rare earth chloride solution to a level of 4.3% by weight  $RE_2O_3$  and

30 impregnated with 3 ppm platinum.

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Example V

A catalyst was prepared by the procedure set forth in Example I, however, the zeolite input consisted of 25% NaY, 25%  $\text{Al}_2\text{O}_3$  as trihydrate, 27% kaolin clay and 23%  $\text{SiO}_2$  as binder.

As in Example IV above, the catalyst slurry was spray dried, followed by washing with ammonium sulfate, exchanged with rare earth chloride solution to a level of 4.5% by weight  $\text{RE}_2\text{O}_3$  and impregnated with 3 ppm platinum.

Example VI

To illustrate the ability of a catalyst of the present inventions to adsorb and fix sulfur oxides at high temperatures, a sample of the catalyst of Example V was compared to a sample of a commercial catalyst (CBZ-1) which comprised rare earths exchanged type Y zeolite in a silica-alumina/clay matrix. The catalyst samples were exposed to a stream of gas which contained 2000 ppm  $\text{SO}_2$ , 4%  $\text{O}_2$  and the balance  $\text{N}_2$  at a temperature of 1150°F for 12 minutes. The catalyst samples were then analyzed for increase in sulfate ( $\text{SO}_4$ ) content. The results are summarized in Table II below.

Table II

<u>Catalyst</u>	<u><math>\text{SO}_4</math> Content (wt %)</u>	
	<u>Before Test</u>	<u>After Test</u>
Of Invention (Example V)	0.3	0.5
Of Prior Art (CBZ-1)	1.0	1.0

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From the above results it is observed that the catalyst of the present inventions have the ability to adsorb  $\text{SO}_2$  at elevated temperatures in the presence of  $\text{O}_2$  and  $\text{N}_2$  whereas the conventional CBZ-1 catalyst does not. In light of this data it is believed that our novel catalysts have the ability to adsorb sulfur oxides in the regeneration section of a commercial fluid catalytic cracking unit. It is also believed that the adsorbed oxides would be reduced to  $\text{H}_2\text{S}$  during the  
10 catalytic cracking cycle, and that the  $\text{H}_2\text{S}$  could be readily recovered from the cracked hydrocarbon gas stream. Therefore, it is concluded that the catalysts of the present invention will have the ability to reduce the emissions of sulfur oxides into the atmosphere.

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WHAT IS CLAIMED IS:

1. A catalytic cracking catalyst which comprises:
  - (a) from about 12 to 60% by weight of Group II to VIII metal exchanged Type Y zeolite;
  - (b) from about 5 to 60% by weight alpha-alumina trihydrate;
  - (c) from about 15 to 40% by weight of an inorganic oxide binder;
  - (d) from about 0.1 to 20 ppm of a noble metal selected from the group consisting of platinum, palladium and mixtures thereof; and
  - (e) from about 0 to balance percent by weight clay;said zeolite, clay, alumina and binder being composited into catalyst particles.
2. The catalysts of Claim 1 wherein said zeolite is selected from the group consisting of REY, PCY, CaREY, REHY, CREY and mixtures thereof.
3. The catalyst of Claim 1 wherein said inorganic binder is selected from the group consisting of silica, alumina, and alumina-silica sols.
4. The catalyst of Claim 3 wherein said binder is present in amounts of from about 15 to 40% by weight of said catalyst.
5. The catalyst of Claim 1 which contains from about 2 to 10 parts per million noble metal.
6. The catalyst of Claim 1 wherein said noble metal is impregnated upon said catalyst particles.
7. The catalyst of Claim 1 wherein said noble metal is impregnated upon a particulate inorganic oxide support which is mixed with said catalyst.
8. The catalyst of Claim 1 wherein said zeolite is REY which contains from about 11 to 22% by weight rare earth ions.

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- 1            9. The catalyst of Claim 1 wherein the  $\text{Na}_2\text{O}$  content thereof is less than 2% by weight.

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